

## The effect of phosphate rock dissolution on soil chemical properties and wheat seedling root elongation

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### Abstract

Soils of the Appalachian region of the United States are acidic and deficient in P. North Carolina phosphate rock (PR), a highly substituted fluoroapatite, should be quite reactive in these soils, allowing it to serve both as a source of P and a potential ameliorant of soil acidity. An experiment was conducted to evaluate the influence of PR dissolution on soil chemical properties and wheat (*Triticum aestivum* cv. Hart) seedling root elongation. Ten treatments including nine rates of PR (0, 12.5, 25, 50, 100, 200, 400, 800, and 1600 mg P kg<sup>-1</sup>) and a CaCO<sub>3</sub> (1000 mg kg<sup>-1</sup>) control were mixed with two acidic soils, moistened to a level corresponding to 33 kPa moisture tension and incubated for 30 days. Pregerminated wheat seedlings were grown for three days in the PR treated soils and the CaCO<sub>3</sub> control. Root length was significantly ( $P < 0.05$ ) increased both by PR treatments and CaCO<sub>3</sub>, indicating that PR dissolution was ameliorating soil acidity. The PR treatments increased soil pH, exchangeable Ca, and soil solution Ca while lowering exchangeable Al and 0.01 M CaCl<sub>2</sub> extractable soil Al. Root growth in PR treatments was best described by an exponential equation ( $P < 0.01$ ) containing 0.01 M CaCl<sub>2</sub> extractable Al. The PR dissolution did not reduce total soil solution Al, but did release Al complexing anions into soil solution, which along with increased pH, shifted Al speciation from toxic to nontoxic forms. These results suggest that North Carolina PR should contribute to amelioration of soil acidity in acidic, low CEC soils of the Appalachian region.

### Introduction

Numerous studies have been conducted to investigate the reactivity and fertilizer effectiveness of phosphate rock (PR) sources in various types of soils (Chien *et al.*, 1987; Hammond *et al.*, 1986; Kanabo and Gilkes, 1988; Smyth and Sanchez, 1982). Recent studies on low buffer capacity acid soils have indicated that certain PRs have both a substantial liming effect and serve as an important source of Ca (Easterwood *et al.*, 1989; Hellums *et al.*, 1989).

Hellums *et al.* (1989) found that even in the presence of adequate added P, medium and high reactivity PR increased dry matter yield and Ca

uptake of maize (*Zea mays* L.) grown in an acid soil with low exchangeable Ca. Easterwood *et al.* (1989) demonstrated that PR (carbonate apatites) from North Carolina and Central Florida applied at a rate of 400 mg P kg<sup>-1</sup> increased pH of a Dothan fine sandy loam (Typic Paleudult) by more than 1 pH unit and substantially lowered exchangeable Al.

Dissolution of carbonate substituted fluoroapatites, such as North Carolina PR, would release basic cations, phosphates, carbonates, and fluoride into soil solution (Easterwood *et al.*, 1989). Dissolution products should have a significant effect on Al activity and speciation in soil solution, and therefore, should contribute to

amelioration of Al toxicity. An improved rooting environment and enhanced root growth should result from PR additions to acid soils. Effects of PR on maize root growth were not reported by Easterwood *et al.* (1989) or Hellums *et al.* (1989).

Short-term (2–4 day) bioassay techniques (Alrichs *et al.*, 1990; Ritchey *et al.*, 1989) which depend upon root development of seedlings in soil have been used to relate soil and soil solution properties to root elongation (Wright *et al.*, 1989a,b). In the bioassay technique, the seed supplies nutrients and only Al toxicity and Ca and B deficiencies limit seedling root elongation. The bioassay technique allows separation of nutritional effects from direct soil acidity effects on root growth and should be useful for monitoring PR effects upon acid soil rooting environments. The current experiment was undertaken to: (1) measure seedling root elongation as a function of PR application rate, and (2) relate changes in soil and soil solution properties resulting from PR additions to root elongation.

## Materials and methods

Acidic subsoil horizons from two major Appalachian hill land soils, Berks (loamy-skeletal, mixed, mesic Typic Dystrochrepts) and Lily (fine-loamy, siliceous, mesic Typic Hapludults), were used in the investigation. Selected properties of the Berks E and Lily Bt horizons are shown in Table 1. The soil horizons were characterized by low pH, low exchangeable Ca, and high exchangeable Al, and when unlimed provide an unfavorable environment for root elongation (Wright *et al.*, 1987).

A reactive, high carbonate-substituted North Carolina PR source containing 131.9 g P kg<sup>-1</sup>

and 352.8 g Ca kg<sup>-1</sup> was used in the investigation. The PR was ground to pass a 150  $\mu$ m sieve and mixed with each soil horizon at rates corresponding to 0, 12.5, 25, 50, 100, 200, 400, 800, and 1600 mg P kg<sup>-1</sup>. A CaCO<sub>3</sub> treatment containing 1000 mg CaCO<sub>3</sub> kg<sup>-1</sup> was included for each horizon to provide a point of comparison for the liming value of the PR. The treated soils were moistened to a level corresponding to 33 kPa tension (Berks E, Pw = 24.3 w/w; Lily Bt, Pw = 19.4 w/w) and allowed to incubate for 30 days at 21°C. At the midpoint of the incubation period, the samples were mixed and moisture adjusted as needed.

At the end of the incubation period, an Al sensitive soft red winter wheat (cv. Hart, Devine Seed Co., Yellow Springs, Ohio) was grown in the 10 treatments of each soil horizon. Details of the bioassay technique have been reported previously (Ritchey *et al.*, 1988). Wheat seeds were pregerminated on moist chromatography paper and five planted into moist soil (bulk density 1.0 Mg m<sup>-3</sup>) in 200 mL plastic cups. Three replications of each soil horizon-treatment combination were arranged in a randomized complete block design. The cups were maintained in high humidity plastic covered containers so that watering would not be required during the three day growth period. The containers were kept in a growth chamber at the following conditions: 23°C, 12-h day length, and illumination of 120  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. The longest root of each seedling was measured at harvest.

Soil solutions were removed from the moist soils by centrifugation (Elkhatib *et al.*, 1987) at harvest. Soil solution pH and electrical conductivity were measured immediately. Total soil solution concentrations of Ca, Mg, K, Na, Al, Mn, Fe, and P were determined by ICP emission spectroscopy. Gradient elution ion chromatog-

Table 1. Selected properties of the soil horizons used in the investigation

Soil horizon	pH (1:1 H <sub>2</sub> O)	Organic C	Clay	Exchangeable			CEC <sup>a</sup>
				Ca	Mg	Al	
		(g kg <sup>-1</sup> )	(cmol kg <sup>-1</sup> )				
Berks E	4.27	18.5	121	0.41	0.20	3.89	5.28
Lily Bt	4.78	6.9	184	0.08	0.03	2.98	3.37

<sup>a</sup> Cation exchange capacity calculated from the summation of exchangeable bases and exchangeable acidity.

raphy was used to determine F, Cl,  $\text{NO}_3$ ,  $\text{SO}_4$ , oxalate, and citrate concentrations in soil solution.

A Chelex 100 resin technique (Cambell *et al.*, 1983; Hodges, 1987) was used to estimate soil solution Al complexed by high-molecular-weight organics (OM-Al). Batches of resin were loaded in the manner described by Campbell *et al.* (1983) until pH and Ca and Mg levels maintained in solution by the resin were similar to those in soil solutions to be analyzed. Soil solutions (5 mL) were shaken with 0.25 g of the appropriate loaded resin, centrifuged, and analyzed for Al. A total resin-soil solution contact time of 60 minutes was used, and Al not taken up by the resin was considered to be OM-Al.

Soil samples were analyzed for soil pH 1:1  $\text{H}_2\text{O}$  and 1:1 0.01 M  $\text{CaCl}_2$ ; exchangeable bases (Thomas, 1982); exchangeable acidity and Al (Yuan, 1959); clay content by the pipette method (Gee and Bauder, 1986); and organic C using a CHN analyzer. Cation exchange capacity (CEC) was calculated by summation of exchangeable bases and exchangeable acidity. Soil Al was extracted with 0.01 M  $\text{CaCl}_2$  (soil:solution = 1:2) using the method of Hoyt and Nyborg (1971).

The extent of PR dissolution in the treatments was estimated in two ways. Soil samples (1 gram) were extracted for 16 hours with 0.5 M NaOH at a soil to solution ratio of 1:100 following a prewash with 1 M NaCl for one hour (Mackay *et al.*, 1986). Phosphorus in the extracts was determined colorimetrically using the phosphomolybdate method (Olsen and Sommers, 1982). In the second technique, one gram soil samples were extracted for one hour with 10 mL of 0.25 M  $\text{BaCl}_2$ -TEA at pH 8.1 to determine increases in soil exchangeable Ca due to PR dissolution (Hughes and Gilkes, 1984). Calcium in the extracts was determined using ICP emission spectroscopy. The extent of dissolution was calculated from the P/Ca ratio in the PR assuming free calcite was not present and congruent dissolution of PR occurred (Kanabo and Gilkes, 1988).

A modified version (Parker *et al.*, 1987) of the GEOCHEM computer program (Sposito and Mattigod, 1980) was used to calculate concentrations and activities of free ions and complexes

in soil solution. Formation constants for mononuclear hydroxy-Al species were from Nordstrom and May (1989), equilibrium constants for Al-citrate complexes from Lopez-Quintella *et al.* (1984), and all other equilibrium constants used in the speciation calculations were from Lindsay (1979). Statistical Analysis System (SAS) programs were used to make ANOVA and mean comparison tests for root lengths and to calculate correlation coefficients and regression equations relating root length to soil and soil solution properties.

## Results and discussion

### Root growth

Wheat seedling root growth was significantly increased by the PR treatments (Table 2). The experiment was repeated for each horizon and similar results were obtained in each trial. The trend of increasing root length with P application rate was apparent even at low rates of PR addition. Significant root length increases ( $P < 0.05$ ) were obtained with application of PR at a rate of 25 mg P  $\text{kg}^{-1}$ . A major increase in root length was observed between the 200 mg P  $\text{kg}^{-1}$  and 400 mg P  $\text{kg}^{-1}$  treatments (Table 2). Root length was significantly increased ( $P < 0.05$ ) by PR application rates up to 800 mg P  $\text{kg}^{-1}$  in both horizons. Root growth was also significantly improved by the  $\text{CaCO}_3$  treatment, indicating that soil acidity constraints were limiting root growth in both horizons. Since seed reserves would have supplied the nutrients needed for the three day growth period, response to PR was apparently related to partial correction of soil acidity through increased soil pH, increased Ca, or amelioration of Al toxicity. The ameliorative effect of PR additions was pronounced. The 800 mg P  $\text{kg}^{-1}$  PR treatment increased root length by up to 506 and 633% in the Berks E and Lily Bt horizons, respectively when compared to the 0 P treatment.

### Phosphate rock dissolution

The extent of PR dissolution, after a 30 day incubation in the two soil horizons, is shown as a function of P application rate in Figure 1. Both

Table 2. Mean length of longest root of "Hart" wheat grown for three days in two soil horizons treated with nine levels of phosphate rock and one level of  $\text{CaCO}_3$

Phosphate rock treatment (mg P kg <sup>-1</sup> )	Mean longest root <sup>a</sup> (cm)			
	Berks E		Lily Bt	
	Trial 1	Trial 2	Trial 1	Trial 2
0	1.8 <sup>h</sup>	2.0 <sup>g</sup>	1.5 <sup>e</sup>	1.2 <sup>e</sup>
12.5	2.3 <sup>gh</sup>	2.4 <sup>fg</sup>	1.9 <sup>de</sup>	1.6 <sup>e</sup>
25	2.7 <sup>fg</sup>	2.4 <sup>fg</sup>	2.4 <sup>d</sup>	1.8 <sup>e</sup>
50	3.0 <sup>f</sup>	2.7 <sup>f</sup>	2.3 <sup>d</sup>	3.4 <sup>d</sup>
100	4.4 <sup>e</sup>	3.7 <sup>e</sup>	2.4 <sup>d</sup>	4.2 <sup>c</sup>
200	5.3 <sup>d</sup>	4.8 <sup>d</sup>	4.9 <sup>c</sup>	6.2 <sup>b</sup>
400	9.5 <sup>b</sup>	8.9 <sup>b</sup>	9.2 <sup>b</sup>	9.1 <sup>a</sup>
800	10.9 <sup>a</sup>	10.0 <sup>a</sup>	9.9 <sup>a</sup>	8.8 <sup>a</sup>
1600	11.3 <sup>a</sup>	10.2 <sup>a</sup>	9.3 <sup>b</sup>	9.1 <sup>a</sup>
$\text{CaCO}_3^b$	8.9 <sup>c</sup>	7.3 <sup>c</sup>	9.2 <sup>b</sup>	8.9 <sup>a</sup>

<sup>a</sup> Means from 3 replications containing 5 plants per replication. Means in a column followed by the same letter are not significantly different at the  $P = 0.05$  level by the LSD test.

<sup>b</sup> 1000 mg  $\text{CaCO}_3$  kg<sup>-1</sup>.

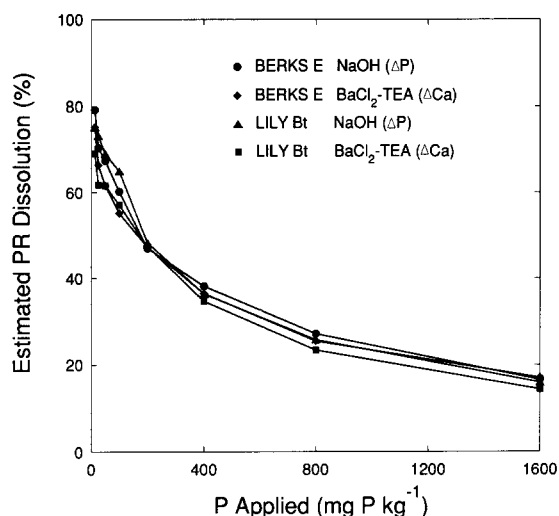


Fig. 1. Estimated dissolution of phosphate rock applied at nine levels to two acidic soil horizons. The samples were incubated for 30 days and phosphate rock dissolution estimated using the NaOH( $\Delta P$ ) and  $\text{BaCl}_2$ -TEA ( $\Delta \text{Ca}$ ) methods.

the NaOH and the  $\text{BaCl}_2$ -TEA extraction techniques resulted in estimated solubilities of PR greater than 60% at P application rates less than 100 mg P kg<sup>-1</sup>. Percent dissolution of PR decreased with increasing application rate. These results are consistent with the findings of Kanabo and Gilkes (1988).

The North Carolina PR showed a similar pat-

tern of high reactivity in both soil horizons (Fig. 1). The estimated dissolution of PR using the NaOH technique varied from 16.5–79.2% and 15.9–75.2% in the Berks E and Lily Bt horizons, respectively. Estimates of PR solubility based on the  $\text{BaCl}_2$ -TEA extraction method ranged from 17.0–75.2% in the Berks E horizon and 14.3–69.1% in the Lily Bt horizon. The NaOH technique estimated slightly higher dissolution of PR at the 12.5, 25, 50, and 100 mg P kg<sup>-1</sup> application rates, but both techniques gave similar results at P application rates  $\geq 200$  mg P kg<sup>-1</sup>. The NaOH technique is based upon the assumption that the reagent does not dissolve the unreacted PR and differences in extractable P ( $\Delta P$ ) between treated and untreated samples represents PR dissolution (Mackay *et al.*, 1986). It is possible that some dissolution of ground PR may have occurred during NaOH extraction, thus leading to somewhat higher PR dissolution estimates. The  $\text{BaCl}_2$ -TEA method characterizes PR dissolution by measuring differences in extractable Ca ( $\Delta \text{Ca}$ ) between treated and untreated samples (Kanabo and Gilkes, 1988). In the absence of free calcite and assuming congruent dissolution of PR,  $\Delta \text{Ca}$  values can be used to calculate P dissolved from PR. Similar results (Fig. 1) were obtained for PR dissolution in both soil horizons using the two independent methods. The high solubility of North Carolina PR in these soils

indicates that it should be useful as a direct application P fertilizer source.

### Soil chemical properties

Soil pH, exchangeable Ca, and soil Ca saturation were significantly increased by PR additions (Table 3). Even at low application rates, the impact on exchangeable Ca was significant. The untreated Lily Bt horizon had low exchangeable Ca ( $0.08 \text{ cmol kg}^{-1}$ ) and part of the root growth increase may have been in response to Ca. Exchangeable Al, soil Al saturation, and soil Al extracted by  $0.01 \text{ M CaCl}_2$  decreased with increasing PR application rate. Extractable Al seemed to be most sensitive to PR addition. It can be noted from Table 3 that the  $\text{CaCO}_3$  treatment ( $1000 \text{ mg kg}^{-1}$ ) was not sufficiently large to completely eliminate soil acidity problems, especially in the Berks E horizon. Root growth (Table 2) in the Berks E horizon was significantly less in the  $\text{CaCO}_3$  treatment than the higher PR treatments.

All soil properties in Table 3 were significantly correlated ( $P < 0.05$ ) with root growth in the two horizons (data not shown). Soil Al extracted by  $0.01 \text{ M CaCl}_2$  proved to be the best predictor of short-term root growth in this experiment. A plot of root length as a function of  $0.01 \text{ M CaCl}_2$ -extractable Al in the Berks E treatments is shown in Figure 2. Previous investigators (Brom-

field *et al.*, 1983; Hoyt and Nyborg, 1971; Jarvis, 1987; Wright *et al.*, 1989b) had reported that  $0.01 \text{ M CaCl}_2$  was an appropriate extractant for identifying Al toxic soils. The amount of Al extracted by  $0.01 \text{ M CaCl}_2$  represents soluble plus some exchangeable Al and should be related to Al in soil solution.

### Soil solution

Soil solution pH was increased 0.43 units and 0.70 units over the range of PR treatments in the Berks E and Lily Bt horizons, respectively (Table 4). Kanabo and Gilkes (1988) attributed soil pH increases resulting from dissolution of PR to consumption of protons during acidulation of PR and subsequent neutralization of bases released. Dissolution of PR greatly increased soil solution Ca in both soil horizons (Table 4). Soil solution Ca was increased 1336% and 6261% by the  $1600 \text{ mg P kg}^{-1}$  treatment relative to the control in the Berks E and Lily Bt horizons, respectively. Calcium could have directly contributed to enhanced root elongation, especially in the Lily Bt horizon, or improved root growth through partial amelioration of Al toxicity (Kinraide and Parker, 1987a).

Total soil solution Al was not reduced by dissolution of PR in either horizon (Table 4) and did not serve as a good predictor of root growth. Fluoride and  $\text{SO}_4$  concentrations in soil solution increased with PR application rate (Table 4). Formation of nontoxic complexes of Al with both F and  $\text{SO}_4$  (Cameron *et al.*, 1986; Kinraide and Parker, 1987b) may have contributed to improved wheat seedling root growth even though total soil solution Al was not decreased. Soil solution P levels increased with PR treatments, but only reached  $19 \mu\text{M}$  in the Berks E treatments and  $28 \mu\text{M}$  in Lily Bt (Table 4). While high concentrations of P and Al may have resulted in precipitation of aluminium phosphates in the vicinity of PR particles, bulk soil solution values were undersaturated relative to precipitation of aluminium phosphate. Approximately 23 and 14% of total soil solution Al (data not shown) in the Berks E and Lily Bt horizons, respectively, was complexed by high molecular weight organics according to estimates made using a Chelex resin technique (Campbell *et al.*,

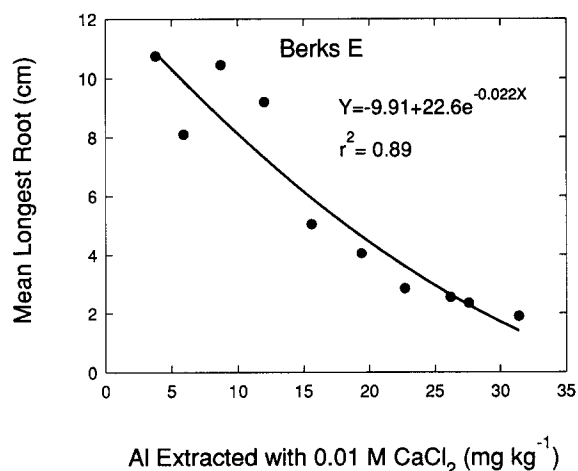


Fig. 2. Mean length of the longest root of three day old wheat seedlings as a function of soil Al extracted by  $0.01 \text{ M CaCl}_2$  from a Berks E soil horizon treated with nine levels of phosphate rock and one level of  $\text{CaCO}_3$ .

Table 3. Effect of phosphate rock treatments on chemical properties<sup>a</sup> in two soil horizons

Phosphate rock treatment (mg P kg <sup>-1</sup> )	Berks E				Lily Bt							
	pH 1:1 H <sub>2</sub> O	Exch. Ca	Exch. Al	Soil Ca Sat. <sup>b</sup>	Soil Al Sat. <sup>c</sup>	Extract. Al <sup>d</sup> mg kg <sup>-1</sup>	pH 1:1 H <sub>2</sub> O	Exch. Ca	Exch. Al	Soil Ca Sat. <sup>b</sup>	Soil Al Sat. <sup>c</sup>	Extract. Al <sup>d</sup> (mg kg <sup>-1</sup> )
0	4.27 <sup>g</sup>	0.41 <sup>i</sup>	3.89 <sup>a</sup>	7.8 <sup>i</sup>	73.6 <sup>a</sup>	31.4 <sup>a</sup>	4.78 <sup>i</sup>	0.08 <sup>j</sup>	2.95 <sup>a</sup>	2.3 <sup>i</sup>	88.6 <sup>a</sup>	36.0 <sup>a</sup>
12.5	4.32 <sup>f</sup>	0.58 <sup>hi</sup>	3.99 <sup>a</sup>	10.3 <sup>h</sup>	72.3 <sup>a</sup>	27.6 <sup>b</sup>	4.85 <sup>h</sup>	0.21 <sup>i</sup>	2.92 <sup>a</sup>	6.1 <sup>h</sup>	85.5 <sup>b</sup>	32.8 <sup>b</sup>
25	4.35 <sup>ef</sup>	0.68 <sup>gh</sup>	3.70 <sup>ab</sup>	12.7 <sup>g</sup>	71.0 <sup>a</sup>	26.2 <sup>c</sup>	4.87 <sup>h</sup>	0.33 <sup>h</sup>	2.88 <sup>a</sup>	9.4 <sup>g</sup>	82.3 <sup>c</sup>	29.0 <sup>c</sup>
50	4.39 <sup>de</sup>	0.91 <sup>g</sup>	3.61 <sup>ab</sup>	16.7 <sup>f</sup>	66.1 <sup>b</sup>	22.7 <sup>d</sup>	4.92 <sup>g</sup>	0.58 <sup>g</sup>	2.62 <sup>b</sup>	16.4 <sup>f</sup>	79.2 <sup>d</sup>	22.6 <sup>d</sup>
100	4.39 <sup>de</sup>	1.32 <sup>f</sup>	3.47 <sup>bc</sup>	23.4 <sup>e</sup>	61.6 <sup>c</sup>	19.4 <sup>e</sup>	4.99 <sup>f</sup>	1.03 <sup>f</sup>	2.26 <sup>c</sup>	28.2 <sup>e</sup>	62.2 <sup>e</sup>	15.3 <sup>e</sup>
200	4.42 <sup>d</sup>	1.90 <sup>e</sup>	3.18 <sup>c</sup>	33.5 <sup>d</sup>	56.1 <sup>d</sup>	15.6 <sup>f</sup>	5.07 <sup>e</sup>	1.65 <sup>e</sup>	1.85 <sup>d</sup>	42.3 <sup>d</sup>	47.4 <sup>f</sup>	10.1 <sup>f</sup>
400	4.55 <sup>c</sup>	2.53 <sup>c</sup>	2.60 <sup>d</sup>	43.0 <sup>c</sup>	44.1 <sup>f</sup>	12.0 <sup>g</sup>	5.19 <sup>d</sup>	2.39 <sup>c</sup>	1.29 <sup>e</sup>	57.8 <sup>c</sup>	31.3 <sup>g</sup>	6.0 <sup>g</sup>
800	4.67 <sup>b</sup>	3.68 <sup>b</sup>	1.80 <sup>e</sup>	60.1 <sup>b</sup>	29.8 <sup>g</sup>	8.7 <sup>h</sup>	5.35 <sup>c</sup>	3.11 <sup>b</sup>	0.83 <sup>f</sup>	70.1 <sup>b</sup>	18.9 <sup>h</sup>	3.0 <sup>h</sup>
1600	4.85 <sup>a</sup>	4.60 <sup>a</sup>	1.00 <sup>f</sup>	72.3 <sup>a</sup>	15.5 <sup>b</sup>	3.8 <sup>j</sup>	5.62 <sup>a</sup>	3.77 <sup>a</sup>	0.43 <sup>g</sup>	79.9 <sup>a</sup>	9.2 <sup>i</sup>	1.1 <sup>j</sup>
CaCO <sub>3</sub> <sup>e</sup>	4.65 <sup>b</sup>	2.29 <sup>d</sup>	2.76 <sup>d</sup>	40.8 <sup>c</sup>	49.2 <sup>e</sup>	5.9 <sup>i</sup>	5.38 <sup>b</sup>	2.18 <sup>d</sup>	1.22 <sup>e</sup>	58.0 <sup>c</sup>	32.4 <sup>g</sup>	2.2 <sup>j</sup>

<sup>a</sup> Mean values from 3 replications.<sup>b</sup> Soil Ca sat. = (Exch. Ca/CEC) 100.<sup>c</sup> Soil Al sat. = (Exch. Al/CEC) 100.<sup>d</sup> 0.01 M CaCl<sub>2</sub>, 16 h shaking, 10 g soil, 20 mL extractant.<sup>e</sup> 1000 mg CaCO<sub>3</sub> kg<sup>-1</sup>.Means in a column followed by the same letter are not significantly different at the  $P = 0.05$  level by the LSD test.

Table 4. Soil solution composition<sup>a</sup> in two soil horizons treated with nine levels of phosphate rock and one level of CaCO<sub>3</sub>

Phosphate rock treatment (mg P kg <sup>-1</sup> )	pH	F	SO <sub>4</sub>	P	Ca	Mg	K	Na	Al	Mn
		( $\mu$ M)								
<i>Berks E</i>										
0	4.58	5.5	442	6.4	218	190	252	223	78	17
12.5	4.53	7.7	538	5.5	292	195	231	413	73	15
25	4.66	10.3	558	5.8	308	169	244	330	69	13
50	4.71	16.3	669	5.4	413	166	220	397	72	12
100	4.62	19.8	881	6.1	644	184	220	389	86	12
200	4.80	34.1	1320	7.4	981	204	186	586	95	11
400	4.75	40.9	1840	10.9	1540	257	219	779	113	11
800	4.86	31.3	2521	13.9	2347	310	221	1042	99	11
1600	5.01	30.5	3269	19.4	3131	378	176	1169	76	7
CaCO <sub>3</sub> <sup>b</sup>	4.93	5.1	757	7.0	841	115	161	190	48	9
<i>Lily Bt</i>										
0	4.82	4.2	143	4.0	69	38	224	313	29	35
12.5	4.79	5.0	193	4.0	112	38	204	312	29	28
25	4.83	5.7	223	5.1	195	43	187	357	30	31
50	4.98	5.3	357	4.6	295	44	141	456	25	26
100	4.85	7.8	626	5.9	509	49	211	519	31	26
200	4.91	11.6	1014	9.0	880	64	139	809	38	28
400	5.10	12.2	1706	9.0	1637	95	113	929	42	29
800	5.27	10.3	3758	16.2	2988	170	117	1121	58	28
1600	5.52	8.2	3996	28.3	4389	290	122	1022	24	22
CaCO <sub>3</sub> <sup>b</sup>	5.54	4.2	564	5.2	797	30	78	201	3	18

<sup>a</sup> Fe, Cl, NO<sub>3</sub>, oxalate and citrate were also measured in soil solutions and utilized in subsequent speciation calculations, but have not been listed in Table 4.

<sup>b</sup> 1000 mg CaCO<sub>3</sub> kg<sup>-1</sup>.

1983; Hodges, 1987). This organically bound Al would be nontoxic and was not included in subsequent speciation calculations.

An estimate of mononuclear Al speciation in soil solution was obtained using the soil solution composition (Table 4) and the modified GEOCHEM program of Parker *et al.*, (1987). Calculated activities of Al species, Ca<sup>2+</sup> and Mg<sup>2+</sup> are shown in Table 5. The activity of Al<sup>3+</sup> ({Al<sup>3+</sup>}) decreased with increasing levels of PR addition (Table 5). Parker *et al.* (1988) demonstrated that, in the absence of Al polymers, {Al<sup>3+</sup>} was the best indicator of wheat seedling root elongation. Although root growth (Table 2) was similar in the Berks E and Lily Bt horizons, calculated {Al<sup>3+</sup>} was much higher in the Berks E horizon treatments (Table 5). Bruce (1990) suggested that the expression of Al toxicity associated with {Al<sup>3+</sup>} was controlled by soil solution ionic strength (I). Berks E soil solutions had higher I values than comparably treated Lily Bt

samples at PR application rates up to 200 mg P kg<sup>-1</sup> (Table 5). The presence of basic cations can also influence the expression of Al toxicity. Kinraide and Parker (1987) demonstrated that Ca and other basic cations can ameliorate Al toxicity. At low PR application rates ( $\leq 200$  mg P kg<sup>-1</sup>) activities of Ca<sup>2+</sup> ({Ca<sup>2+</sup>}) and Mg<sup>2+</sup> ({Mg<sup>2+</sup>}) were much greater in the Berks E than the Lily Bt soil solutions. Therefore, Al toxicity would probably be expressed at lower {Al<sup>3+</sup>} in the Lily Bt treatments. Overall, PR dissolution greatly increased {Ca<sup>2+</sup>} in soil solution in both horizons (Table 5). The {Ca<sup>2+</sup>}/{Al<sup>3+</sup>} ratio increased from 9 to 468 and 8 to 5415 in the Berks E and Lily Bt treatments, respectively, with increasing PR application rate.

Dissolution of PR increased fluoride and sulfate concentrations in soil solution (Table 4) and resulted in the formation of Al-F and Al-SO<sub>4</sub> complexes (Table 5). Both Al-F and Al-SO<sub>4</sub>

Table 5. Activities of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and Al species<sup>a</sup> in soil solution, and ionic strength as calculated by the GEOCHEM program

Phosphate rock treatment (mg P kg <sup>-1</sup> )	$\text{Ca}^{2+}$ ( $\mu\text{M}$ )	$\text{Mg}^{2+}$	$\text{Al}^{3+}$	$\text{Al}(\text{OH})^{2+}$	$\text{Al}(\text{OH})_2^+$	$\text{AlF}^b$	$\text{AlSO}_4^c$	Ionic strength m M
<i>Berks E</i>								
0	165	146	18	6.8	2.1	4.4	9.7	2.6
12.5	217	146	15	5.2	1.4	6.0	9.8	2.9
25	229	127	12	5.5	2.0	7.9	8.1	2.8
50	299	122	10	5.2	2.2	12	8.2	3.2
100	447	130	13	5.4	1.8	15	13	4.1
200	636	135	9.0	5.7	2.8	23	13	5.5
400	929	159	10	5.7	2.6	27	20	7.5
800	1309	178	7.4	5.4	3.1	20	18	10
1600	1637	204	3.5	3.5	2.9	18	10	13
$\text{CaCO}_3^d$	594	83	5.3	4.5	3.0	3.7	4.5	3.8
<i>Lily Bt</i>								
0	57	32	7.2	4.8	2.5	3.4	1.3	1.4
12.5	93	31	7.6	4.7	2.3	4.1	1.9	1.3
25	157	35	6.4	4.3	2.3	4.6	1.8	1.7
50	230	35	4.2	4.0	3.1	4.1	1.9	2.1
100	370	36	4.5	3.2	1.8	5.8	3.4	3.1
200	595	44	4.7	3.8	2.5	8.2	5.4	4.5
400	1001	60	3.4	4.4	4.3	8.0	6.1	7.1
800	1511	90	2.7	5.0	7.5	6.1	9.7	13
1600	2166	149	0.4	1.3	3.4	4.1	1.3	15
$\text{CaCO}_3^d$	583	23	0.0	0.0	0.0	0.3	0.0	3.2

<sup>a</sup> Summation of the activities of Al complexes with citrate and oxalate were  $\leq 2.7 \mu\text{M}$  for Berks E treatments and  $\leq 2.0 \mu\text{M}$  for Lily Bt treatments. These values are not listed in Table 5.

<sup>b</sup>  $\text{AlF} = \text{AlF}^{2+} + \text{AlF}_2^+ + \text{AlF}_3^0$

<sup>c</sup>  $\text{AlSO}_4 = \text{AlSO}_4^+ + \text{Al}(\text{SO}_4)_2^-$

<sup>d</sup> 1000 mg  $\text{CaCO}_3 \text{ kg}^{-1}$ .

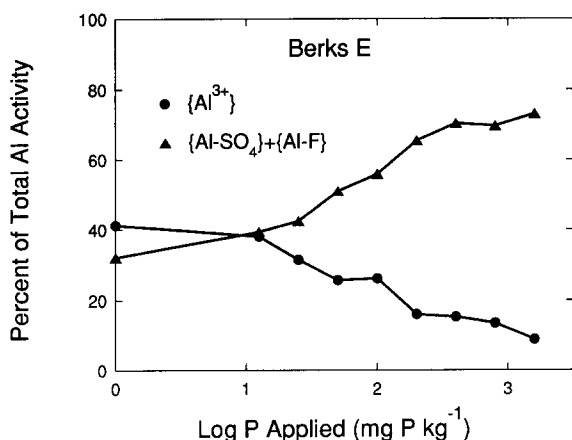


Fig. 3. Changes in the distribution of  $\{\text{Al}^{3+}\}$  and  $\{\text{Al-SO}_4\} + \{\text{Al-F}\}$  in soil solution as a function of application rate of phosphate rock (expressed as  $\log_{10}$  P applied) to the Berks E soil horizon. Values of  $\{\text{Al}^{3+}\}$  and  $\{\text{Al-SO}_4\} + \{\text{Al-F}\}$  are given as a percentage of total Al activity in soil solution.

complexes have been shown to be nontoxic to plants (Cameron *et al.*, 1986; Kinraide and Parker 1987b). The distribution of  $\{\text{Al}^{3+}\}$  and  $\{\text{Al-SO}_4\} + \{\text{Al-F}\}$  in Berks E soil solutions is shown as a function PR application rate in Figure 3. The  $\{\text{Al}^{3+}\}$  dropped from 41 to 9% of total soil solution Al activity, and  $\{\text{Al-SO}_4\} + \{\text{Al-F}\}$  increased from 32 to 73% of total soil solution Al activity across the range of PR additions. While PR dissolution did not reduce total soil solution Al (Table 4), it did result in a shift of Al speciation from toxic to nontoxic forms.

## Summary

North Carolina PR was quite reactive in acidic soil horizons used in this study. Partial dissolu-



tion of the PR increased soil pH, exchangeable Ca and soil solution Ca while lowering exchangeable Al and soil Al extracted by 0.01M CaCl<sub>2</sub>. Although total soil solution Al was not reduced by PR treatments, {Al<sup>3+</sup>} was decreased and nontoxic Al-F and Al-SO<sub>4</sub> complexes were formed. These improvements in soil chemical properties and shifts in soil solution Al speciation from toxic to nontoxic forms resulted in enhanced root growth of wheat seedlings. Direct application of North Carolina PR should contribute to amelioration of soil acidity in acidic, low CEC soils of the Appalachian region.

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